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Request for grant of a patent

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The Patent Office

Cardiff Road
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Gwent NP9 1RH

Your reference	BKCD/NS/DBN.105(a) 14 JAN 2000
Patent application number *(The Patent Office will fill in this part)*	0000780.7
Full name, address and postcode of the or of each applicant *(underline all surnames)*	Trikon Holdings Limited Coed Rhedyn Ringland Way Newport, Gwent NP6 2TA
Patents ADP number *(if you know it)*	7435423001
If the applicant is a corporate body, give the country/state of its incorporation	
Title of the invention	A Method of Processing a Polymer Layer
Name of your agent *(if you have one)*	Wynne-Jones, Laine & James
"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	22 Rodney Road Cheltenham GL50 1JJ
Patents ADP number *(if you know it)*	1792001

If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day / month / year)*

Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

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Continuation sheets of this form	
Description	6
Claim(s)	0
Abstract	0
Drawing(s)	6 7

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature: Wynne-Jones, Laine & James — Date: 14.01.2000

12. Name and daytime telephone number of person to contact in the United Kingdom: Mr. B. Dunlop — 01242 515807

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A Method of Processing a Polymer Layer

In our pending British Patent Application 9922801.7, which is incorporated herein by reference we discuss the use of a plasma treatment during the step of heating a polymer layer to desorb moisture and harden the layer and exposing the layer to a plasma during that heating process. In the preliminary discussion, it was perceived that the main benefit of this procedure was to reduce cracking in the polymer layer, but it was noted that the plasma treatment was significantly changing the film structure as shown by the FTIR.

It has now been established that further surprising benefits can be obtained if low k films are treated in this manner and these will be described in connection with the following drawings in which:

Figure 7 and 8 plot dielectric constant against plasma heating time at various temperatures and generally correspond with Figure 4;

Figures 9 to 12 illustrate the effect of strip process on k-value; and Figure 13 indicates k value stability.

It will be again seen from Figures 7 and 8, that combination of heat and plasma exposure time affect the k-value achieved for example a 3 minute plasma exposure at

350°C or a 2 minute exposure at 400°C appear particularly efficacious.

Looking at the benefits of the treated films the wet etch rate of hydrogen treated films using a 10:1 BOE (buffered oxide etch) at 20°C are typically similar to or less than that of thermal oxide i.e. around 550 Å/min. The untreated films etch at over 10,000 Å/min. Accordingly the hydrogen plasma treatment therefore reduces the wet etch rate by a factor of 20 or more. Wet etch rate is generally used as an indication of merit for silicon dioxide layers where thermal oxide is considered to be of high quality.

It has been determined that hydrogen plasma treatment is effective to varying depths dependent on the time of the process and the composition of the film. In general the lower the k value the greater the depth of treatment. Thus for a k=2.7 film, the treatment penetrated to a depth of 3,000 Å whilst with a K=2.4 film the depth of treatment was 5,700 Å. Both tests were carried out under the following conditions:

Hydrogen Flow	1000 sccm
Platen Temperature	400°C
RF Power	1000 Watts
RF Frequency	13.56 MHz
Pressure	4 Torr
Electrode Spacing	6mm
Time	300 seconds

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It has been found that increasing the power level or changing the electrode spacing does not significantly increase the effective depth of the plasma treatment, but increasing the treatment time to 600 seconds increases the depth of treatment on the K=2.7 film from 3000 Å to 6000 Å. (i.e. twice the time, twice the depth).

It will have been noted from our earlier application that the hydrogen treatment also improves, i.e. lowers, the k value. It was considered desirable to determine whether this k value improvement could be achieved for the bulk of the material, even if only a surface treatment took place. Accordingly a 6000 Å, k=2.7 film was formed first by depositing two 3000 Å layers, each of which were treated with a hydrogen plasma for 300 seconds. Secondly 6000 Å layers were deposited and treated for either 300 or 600 seconds. No variation in k value was determined. This appears to show that the film that was only treated to half its depth is still yielding an improved k value of the previous best known method of a vacuum thermal process, which is presumed to give a bulk effect. It is thus postulated that the hydrogen plasma is effective at reducing k values even as a surface treatment perhaps by reducing the likelihood of water re-absorption whilst the

applied heat may be a bulk effect performing the bulk moisture disorption from the as-deposited layer. They hydrogen plasma clearly changes the bonding composition as evidenced by the FTIR data yielding an as-treated layer that etches slower and providing a treated layer that protects the underlying part of the layer from subsequent plasma etch processes and presumably water re-absorption. Thus the hydrogen plasma is effective on a heated layer at improving at least a surface of that layer to the benefit of the whole layer, the improvement being an improvement in the layers usefulness as a low k dielectric in a semiconductor device.

It had previously been found that if the low k films were subjected to oxygen based resist stripping process necessary if low k films are to be integrated into subtractive and damascene schemes using standard processes then carbon tended to be stripped out of the films and presumably replaced by water accompanied by a substantial increase in the k value.

Although Figures 5 and 6 of British Application 9922801.7 indicate that the C-H and SiH bonds are reduced by the hydrogen plasma, resultant structure appears to be stable under strip process.

Thus turning to Figures 9 to 12 the integrated peak area rations for the various indicated bonds are not changed substantially by an oxygen based stripping process. Similarly the effects of the oxygen and hydrogen (reducing) resist strips are shown on the hydrogen plasma treated films reactive indexes in Figures 11 and 12. Refractive index is an indirect indication of k value.

The hydrogen plasma treatment is thus shown to provide an effective barrier to a subsequent oxygen-based plasma process.

In order to ascertain the stability of the k value wafers were blanket coated in a k=2.7 Si-C polymer and were then subjected to a standard flourine based dielectric etch process, followed by a hydrogen plasma (reducing) resist strip process to simulate conditions on the exposed parts of a patterned etched dielectric structure. The dielectric constant was shown (see Figure 13) to remain at 2.7 after these etch and strip processes and to be stable over time. After 48 hours the k value had increased slightly. A 450°C anneal brought the k value back down to 2.7 and after a further 48 hours the k value had increased only very slightly.

The improvement in the surface layer of the low k dielectrics such that its wet etch rate equates to that of

a thermal oxide may be particularly advantageous in connection with chemical mechanical polishing. The mechanical/chemical abrasion of low k dielectrics of the nano-porous and/or carbon containing kind presents a problem as they are typically of low density and have poor mechanical strength. Attempts to chemical mechanical polish such layers tends to cause dishing of the dielectric between the areas of metalisation. This should be less apparent with low k films which have been treated according to the invention.

The advantage of using a hydrogen plasma on a heated wafer were also recognised in our co-pending application No. 99044273. This in particular indicates that hydrogen mixed with etch gas may maintain or enhance the low k structure during etching. It would therefore be particularly advantageous to use that approach when etching materials prepared in accordance with 9922801.7 or this application.

It has also been appreciated that if the surface of the low k material is treated as described in 9922801.7 or this application then it will be possible in at least certain cases to dispense with the capping layer that has been used to date and thus compensate for the rather long cycle times which were mentioned in 9904427.3.

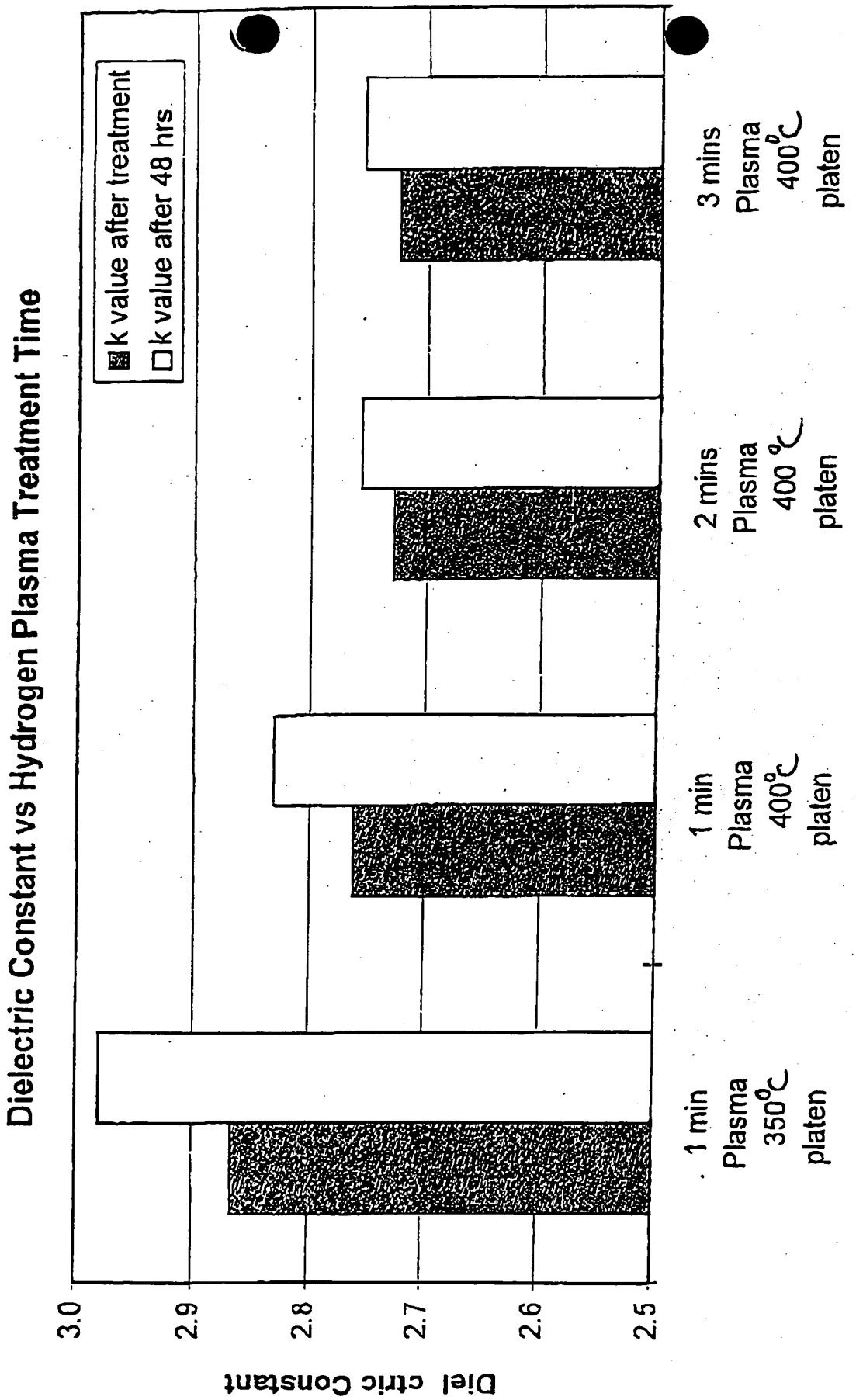

Dielectric Constant vs Hydrogen Plasma Treatment Time
k value after treatment
k value after 48 hrs
Diel ctric Constant
3.0
2.9
2.8
2.7
2.6
2.5
1 min Plasma 350°C platen
1 min Plasma 400°C platen
2 mins Plasma 400°C platen
3 mins Plasma 400°C platen

FIG 7

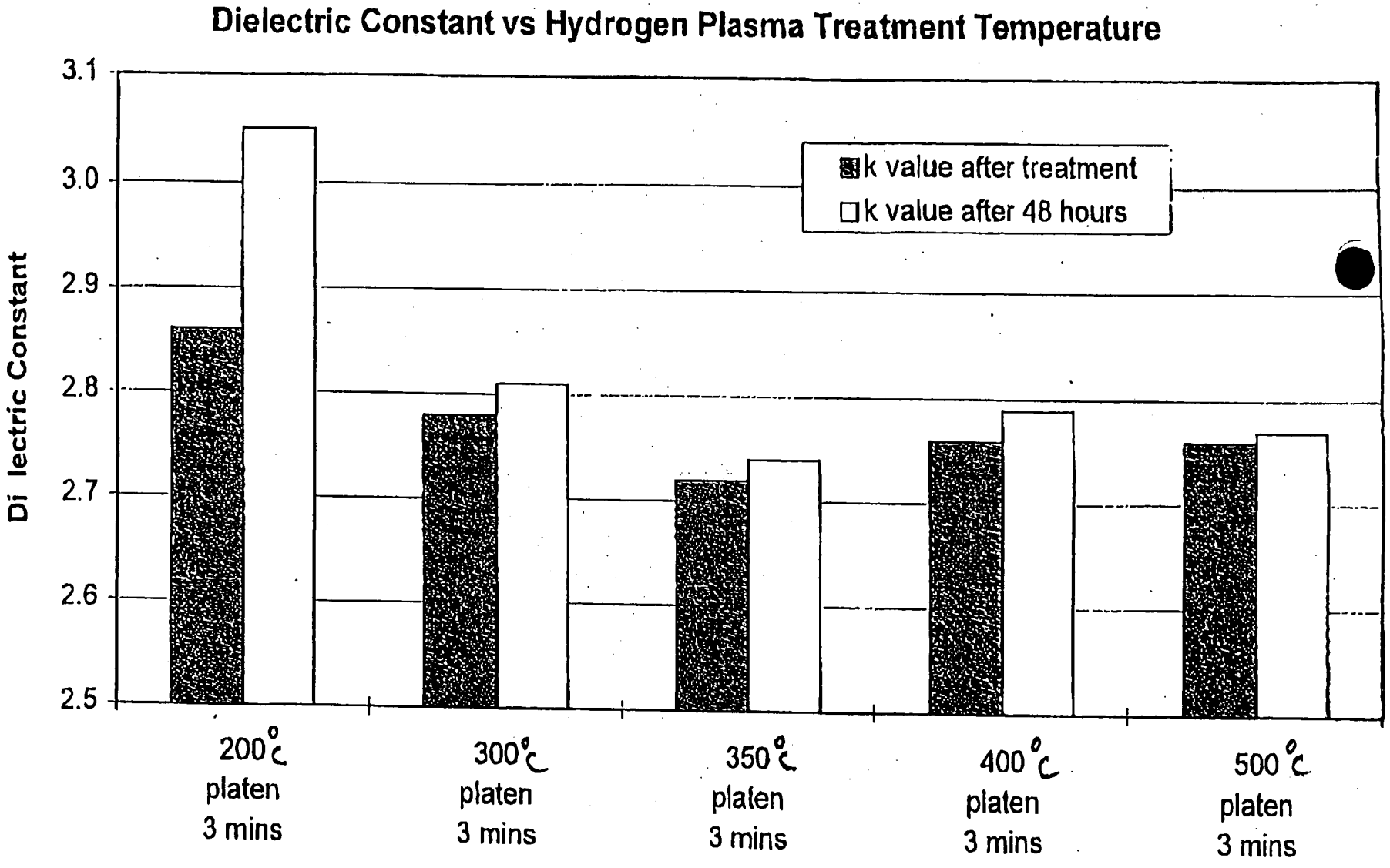
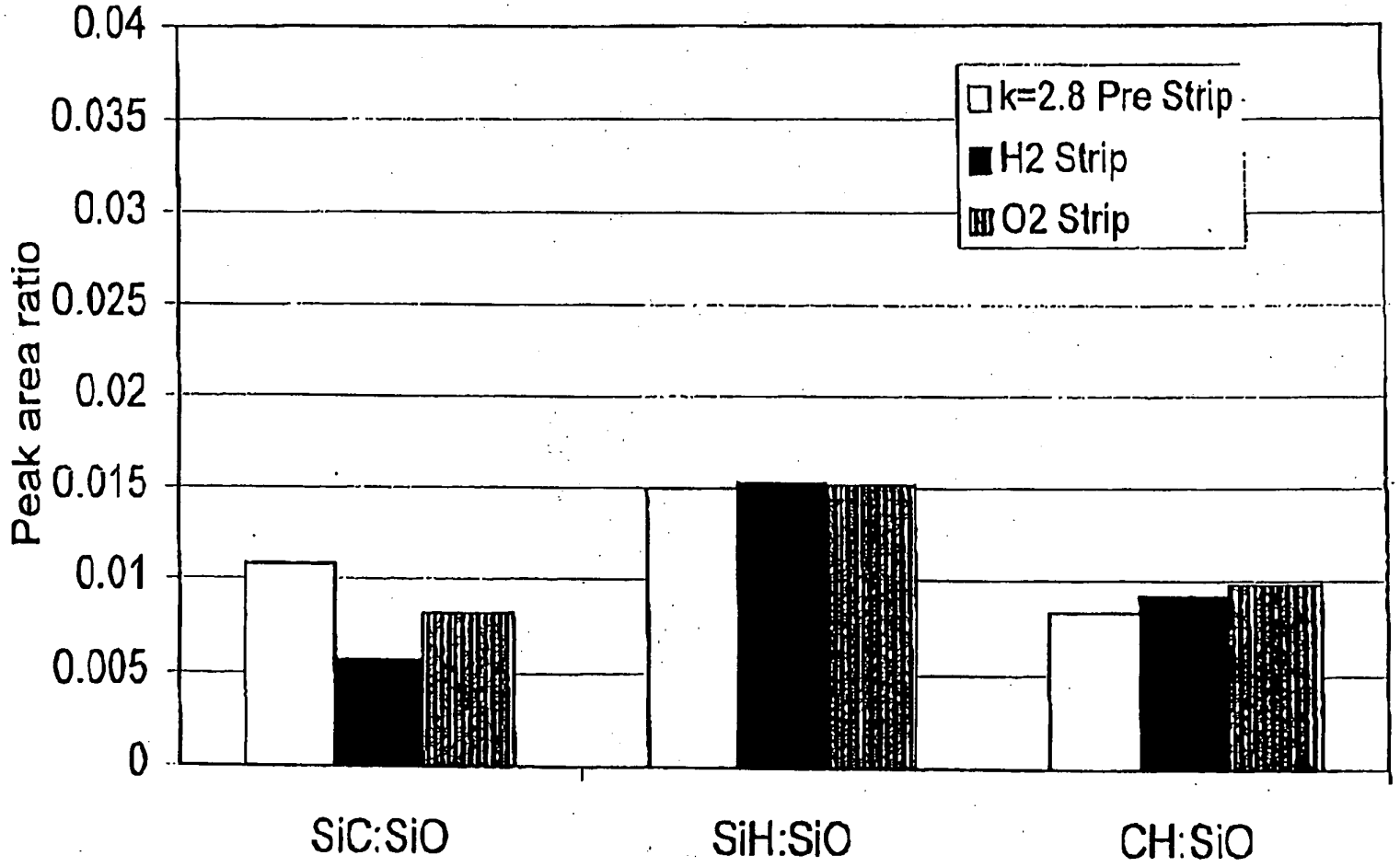
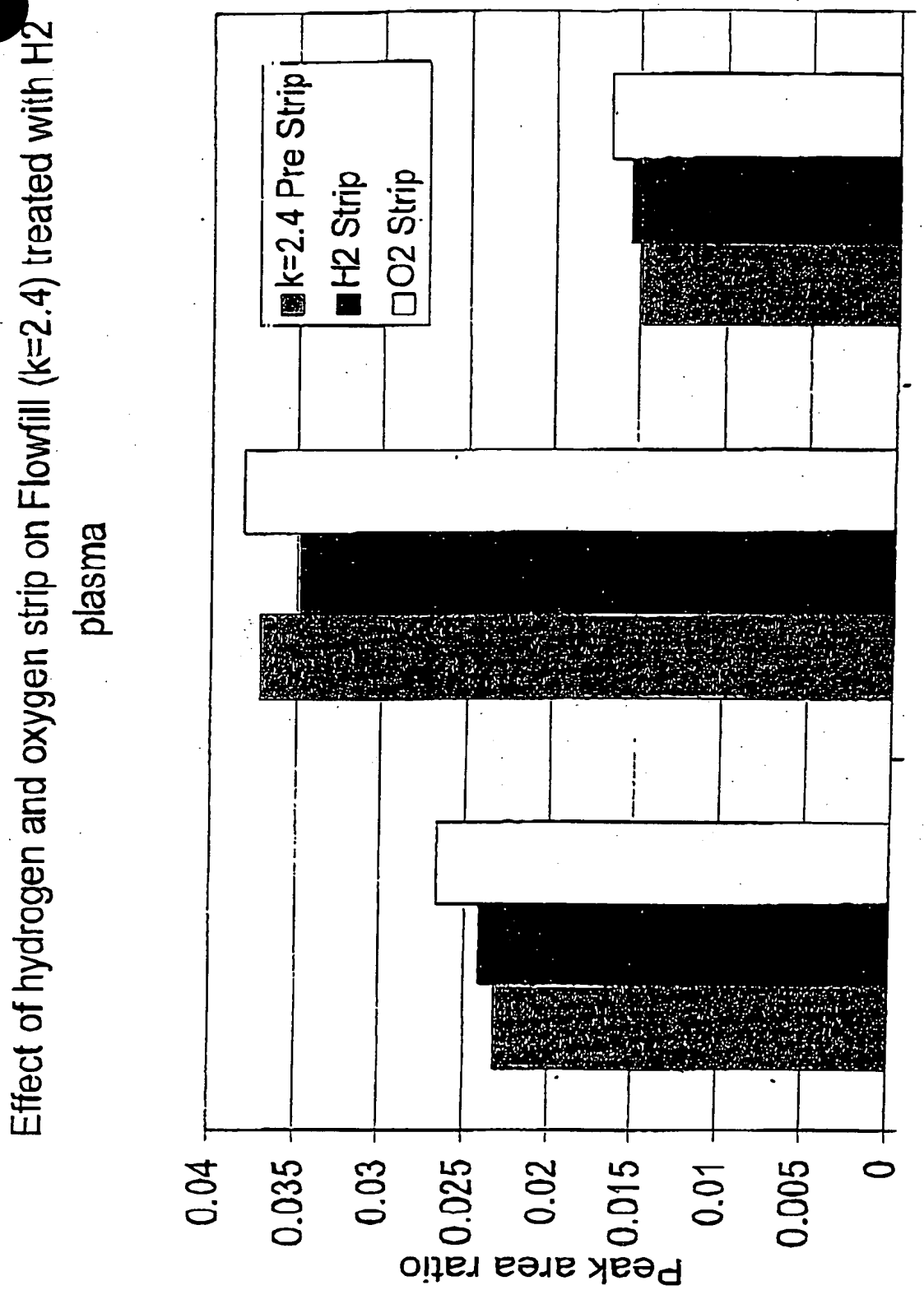


FIG 8



Integrated peak area ratios

FIG9



Integrated peak area ratios

FIG 10

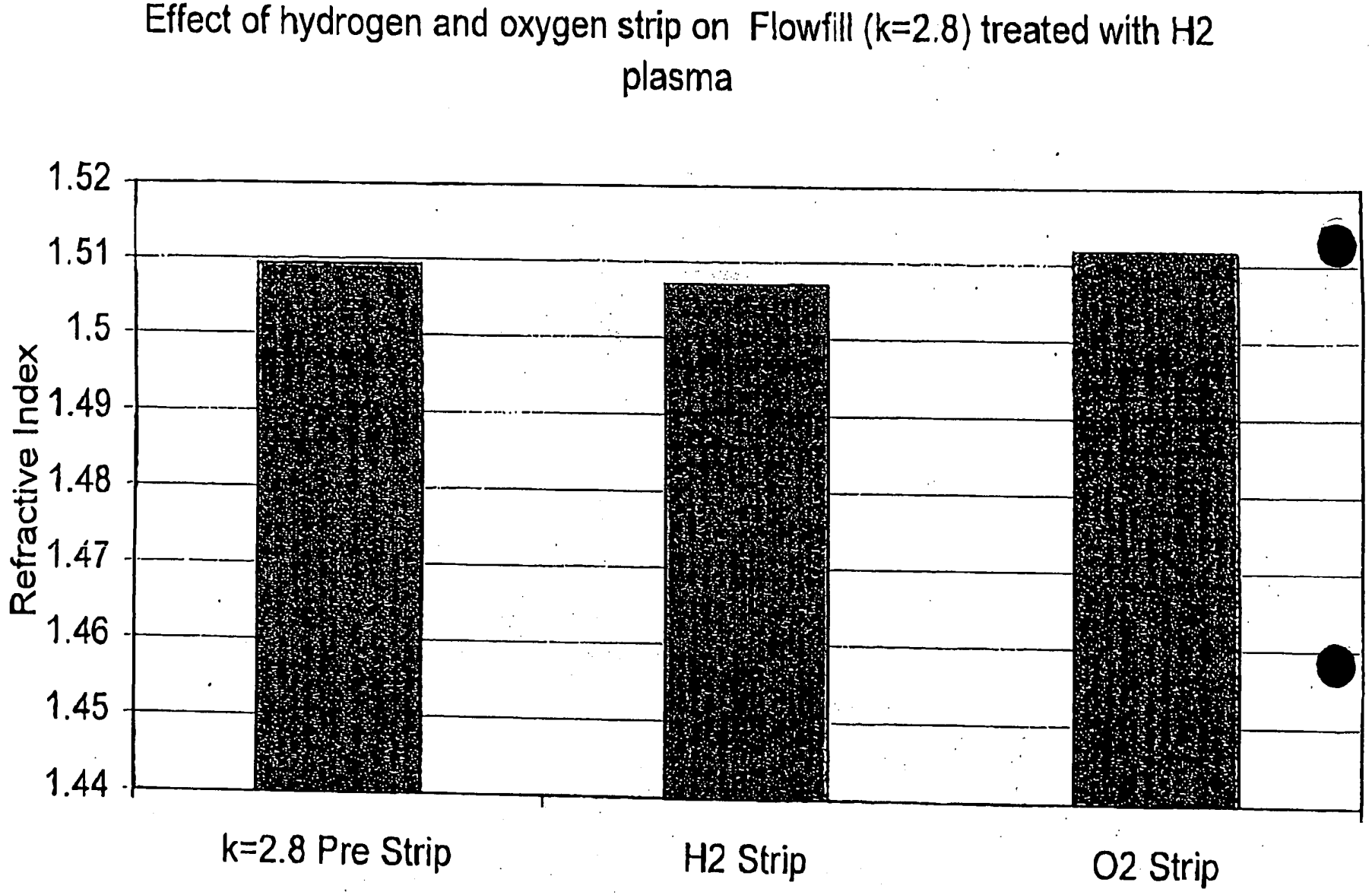


FIG 11

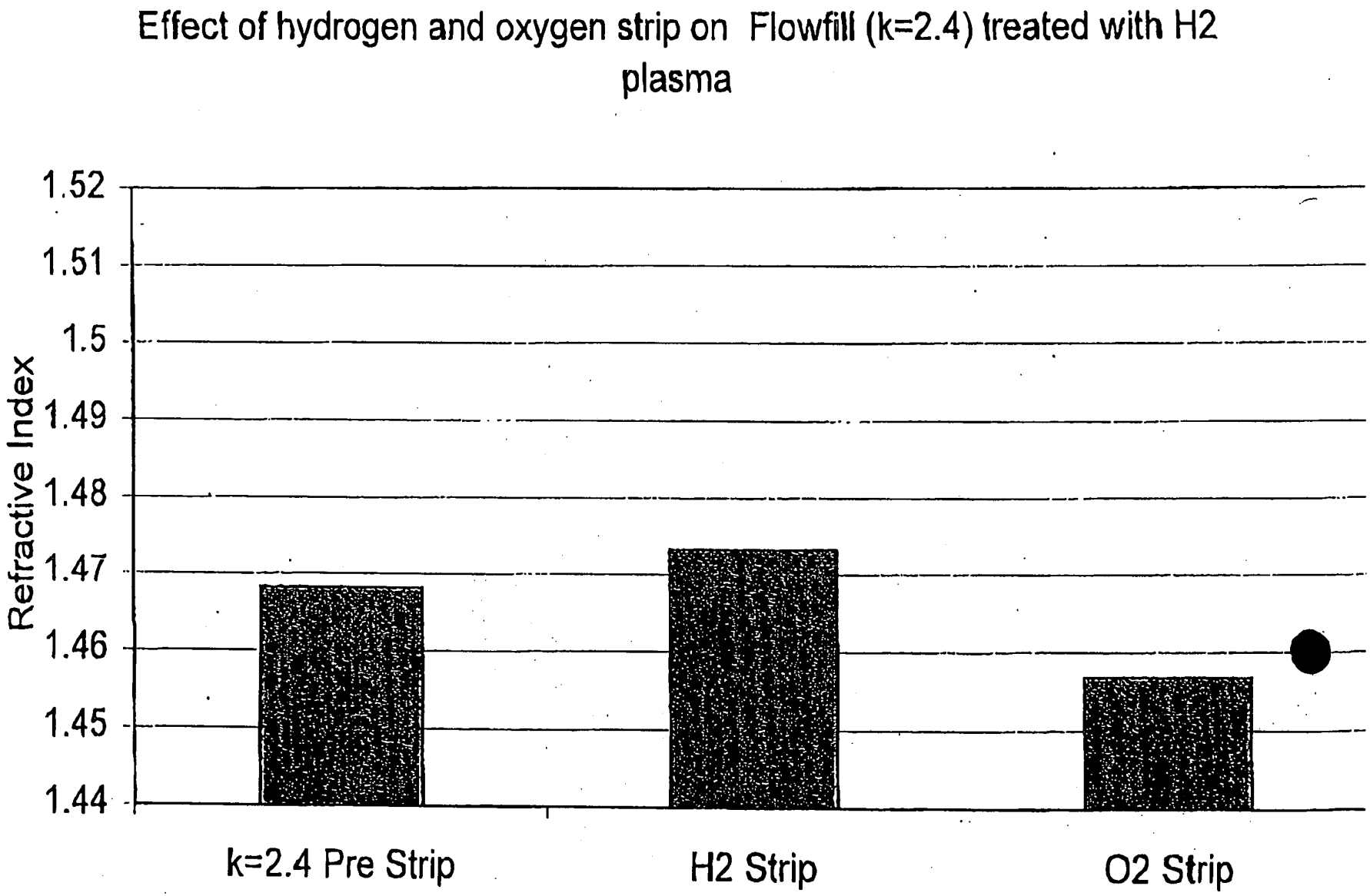


FIG 12

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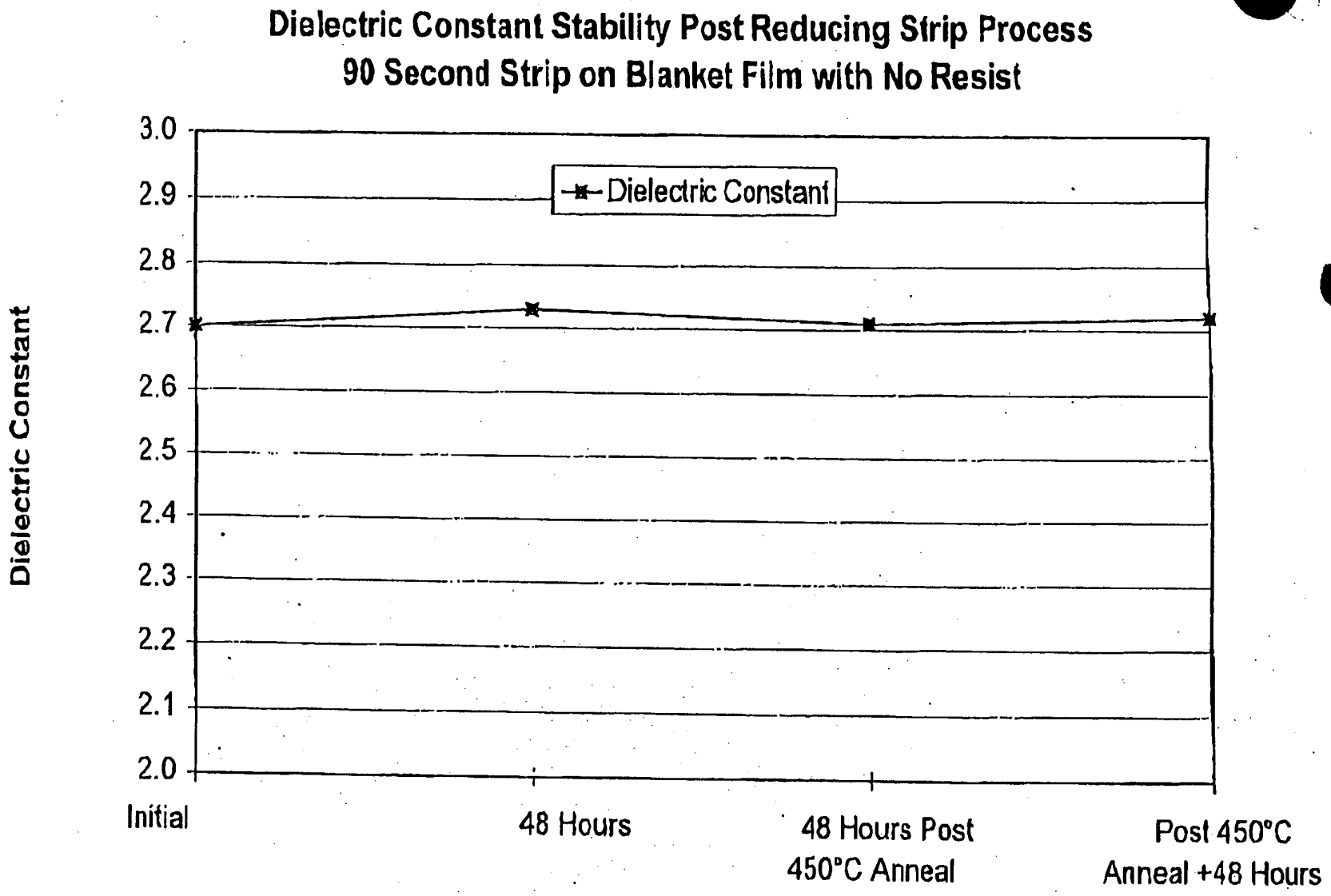

FIG 13.

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Wynne-Jones Laine & James